THE STABILITY OF ORGANIC-CLAY MINERAL COMPLEXES TO ENZYMATIC AND CHEMICAL REACTIONS

BY

ANTON EARL ERICKSON

B. S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

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ACKNOWLEDGMENT

The author appreciates the suggestions, criticisms, and encouragement of Dr. John E. Gieseking, under whose supervision this investigation was made. He is grateful to Dr. R. S. Smith for his interest and co-operation and to Mr. S. A. Watson for his assistance with the apparatus.

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THE STABILITY OF ORGANIC-CLAY MINERAL COMPLEXES TO ENZYMATIC AND CHEMICAL REACTIONS

The interaction of the organic and inorganic soil components has a marked effect on the physical and chemical properties of the soil. Many of these effects can be partly attributed to the organic-clay complex. In recent years, the organic-clay complex has been the object of considerable research. Gieseking and Ensminger have studied the protein-clay mineral complex in some detail and in one study tested the protein complexes to the enzymatic hydrolysis of pepsin and pancreatin.

It was the purpose of this investigation to extend these studies. It was thought that by using simpler molecules whose structures are known, some of the finer details of the organic-clay complexes might be found. To accomplish this, the stability of montmorillonite complexes of amino acids and related compounds were tested by the use of enzymatic and chemical reactions.

Tyrosinase, urease, arginase and amino acid decarboxylase were used for the enzymatic reactions. These enzymes were prepared from potato peelings, jack bean meal, beef liver and a culture of Eschericia coli respectively. In order to test the stability of the complexes, digestions of the plain organic compound and digestions of the organic-montmorillonite complexes were made simultaneously in a Warburg manometric apparatus. Tyrosinase was used to test the stability of one symmetry montmorillonite complexes of tyrosine, para-cresol, phenol, and catechol. The urea complexes were tested by urease with and without an excess of buffer ions. Arginine-montmorillonite complexes were tested against arginase action. Amino acid decarboxylase was used on montmorillonite complexes of arginine, lysine,

and glutamic acid. The enzymatic reactions were performed paying special attention to the control of pH, inhibitors, activators, concentrations, etc. Thus, the activity of the enzyme on the organic compound in the presence of a suitable buffer compared with the activity of the enzyme on the same organic compound sorbed on montmorillonite was considered a measure of the stability of the organic-clay complex.

The Van Slyke amino nitrogen determination, the ninhydrin reaction, and the Dakin and West reaction were used to test the stability of the clay complexes to chemical reactions. Tyrosine- and glycine-montmorillonite complexes were subjected to the action of nitrous acid using the conventional Van Slyke apparatus and procedure. Alanine- and arginine-montmorillonite complexes in the moist and dry condition were reacted with ninhydrin at pH 2.5 at 100°C. The completeness of reaction with the complexes compared to the completeness of reaction with the amino acids alone was used as the measure of the stability of the amino acid-clay complex.

Amino acid-clay complexes were subjected to the action of acetic anhydride in the presence of pyridine at a temperature of 100°C. as described by Dakin and West. Apparatus was assembled so that the amino acid alone and its complex could be reacted simultaneously and the rate of their reactions followed. Montmorillonite complexes of glycine, alanine, glutamic acid and tyrosine were tested. Comparisons were also made with a tyrosine-kaolinite complex and with tyrosine-montmorillonite complexes which contained various proportions of amino acid to clay. Comparisons were made of the effects of different amino acids, kind of clay, and proportions of clay to amino acid on the stability of the clay complexes.

The following conclusions were drawn from this investigation:

Amino acid-montrillonite complexes exhibit a stability to tyrosinase, arginase and amino acid decarboxylase. This stability depends on the enzyme and the amino acid used in the complex. The arginine complex is more stable toward amino acid decarboxylase than toward arginase. Lysine and arginine complexes are more stable than the glutamic acid complexes toward amino acid decarboxylase.

The amino acid group is responsible for the stability of the complexes. The tyrosine complex is stable toward tyrosinase while para-cresol and catechol complexes are only slightly stable and the phenol complex is unstable.

The equilibrium between the inorganic buffer and small organic molecules can help the enzymatic reaction go to completion. The urea in the urea-montmorillonite complex is slowly but completely decomposed by urease in the presence of an excess of buffer ions.

Under certain conditions, the clay seems to catalyze the enzymatic reaction. Tyrosine and para-cresol overcome the "initial lag" in their tyrosinase oxidation which is probably due to weak sorption on the clay.

The stability of the amino acid-clay complexes toward the Dakin and West reaction depends on the kind and amount of amino acid and the kind of clay in the complex. The tyrosine- and alanine-montmorillonite complexes were more stable than the glycine and glutamic acid complexes. The tyrosine-montmorillonite complexes made with one half to two symmetries of tyrosine had about the same per cent stability while the four symmetry complex was slightly less stable. The tyrosine-kaolinite complex was less stable than the montmorillonite complex.

Amino acid-montmorillonite complexes are not stable toward the conditions of the Van Slyke amino nitrogen and ninhydrin reactions.

VITA

The author was born June 5, 1919, in Chicago, Illinois. He attended Bateman Grammar School, Von Steuben Junior High School, and Roosevelt Senior High School of Chicago, where he graduated in June, 1937. In the fall of 1937, he entered the University of Illinois. He received his Bachelor of Science degree in Agriculture with high honors in June, 1941.

In July, 1941, he was employed as a part time Assistant in Soil Survey at the University of Illinois. During the summer of 1942, the author was employed as Assistant Ground Water Geologist for the Illinois State Water Survey. Since the fall of 1942, he has been Assistant and First Assistant in the Soil Survey at the University of Illinois.

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PUBLICATION

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